

Claims

What is claimed is:

1. A method for bonding a fibrous substrate surface to a second substrate surface  
5 comprising:

- (a) providing a catalyst at the fibrous substrate surface;
- (b) contacting the catalyst on the fibrous substrate surface with a metathesizable material so that the metathesizable material undergoes a metathesis reaction; and
- (c) contacting the fibrous substrate surface with a second substrate surface.

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2. A method according to claim 1 wherein the fibrous substrate comprises polyester, nylon or polyamide.

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3. A method according to claim 2 wherein the second substrate surface comprises an elastomeric substrate.

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4. A method according to claim 3 wherein the elastomeric substrate is selected from the group consisting of natural rubber, polychloroprene, polybutadiene, polyisoprene, styrene-butadiene copolymer rubber, acrylonitrile-butadiene copolymer rubber, ethylene-propylene copolymer rubber, ethylene-propylene-diene terpolymer rubber, butyl rubber, brominated butyl rubber, alkylated chlorosulfonated polyethylene rubber, hydrogenated nitrile rubber, poly(n-butyl acrylate), thermoplastic elastomer and mixtures thereof.

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5. A method according to claim 3 wherein the elastomeric substrate is natural rubber or ethylene-propylene-diene terpolymer rubber.

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6. A method according to claim 1 wherein step (a) comprises soaking the fibrous substrate in a catalyst solution and step (b) comprises dipping the catalyst-soaked fibrous substrate into a metathesizable material and allowing polymerization.

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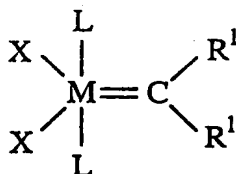
7. A method according to claim 1 wherein step (c) comprises placing the fibrous substrate between two layers of second substrate surface in a mold and curing the second substrate surface with heat and pressure.

8. A method according to claim 1 wherein the catalyst is dissolved or mixed into a liquid carrier fluid.

9. A method according to claim 1 wherein the catalyst is included as a component of the first fibrous substrate.

10. A method according to claim 1 wherein the catalyst is selected from at least one of a rhenium compound, ruthenium compound, osmium compound, molybdenum compound, tungsten compound, titanium compound, niobium compound, iridium compound and  $\text{MgCl}_2$ .

11. A method according to claim 10 wherein the catalyst has a structure represented by



wherein M is Os, Ru or Ir; each  $\text{R}^1$  is the same or different and is H, alkenyl, alkynyl, alkyl, aryl, alkaryl, aralkyl, carboxylate, alkoxy, allenylidenyl, indenyl, alkylalkenylcarboxy, alkenylalkoxy, alkenylaryl, alkynylalkoxy, aryloxy, alkoxycarbonyl, alkylthio, alkylsulfonyl, alkylsulfinyl, amino or amido; X is the same or different and is either an anionic or a neutral ligand group; and L is the same or different and is a neutral electron donor group.

12. A method according to claim 11 wherein X is Cl, Br, I, F, CN, SCN,  $\text{N}_3$ , O-alkyl or O-aryl; L is a heterocyclic ring or  $\text{Q}(\text{R}^2)_a$  wherein Q is P, As, Sb or N;  $\text{R}^2$  is H, cycloalkyl, alkyl, aryl, alkoxy, arylate, amino, alkylamino, arylamino, amido or a heterocyclic ring; and a is 1, 2 or 3; M is Ru; and  $\text{R}^1$  is H, phenyl,  $-\text{CH}=\text{C}(\text{phenyl})_2$ ,  $-\text{CH}=\text{C}(\text{CH}_3)_2$  or  $-\text{C}(\text{CH}_3)_2(\text{phenyl})$ .

13. A method according to claim 10 wherein the catalyst is a phosphine-substituted, an imidazolylidene-substituted, or a dihydroimidazolylidene-substituted ruthenium carbene.

14. A method according to claim 13 wherein the catalyst is  
bis(tricyclohexylphosphine)benzylidene ruthenium (IV) dichloride,  
tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-  
dihydroimidazol-2-ylidene][benzylidene]ruthenium (IV) dichloride, or  
5 tricyclohexylphosphine[1,3-bis(2,3,6-trimethylphenyl)-4,5-imidazol-2-  
ylidene][benzylidene]ruthenium (IV) dichloride.

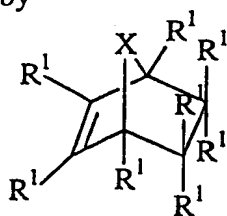
15. A method according to claim 1 wherein the catalyst is stable in the presence  
of moisture and oxygen and can initiate polymerization of the metathesizable material  
10 upon contact at room temperature.

16. A method according to claim 1 wherein the metathesizable material is  
selected from ethene,  $\alpha$ -alkene, acyclic alkene, acyclic diene, acetylene, cyclic alkene,  
cyclic polyene and mixtures thereof.

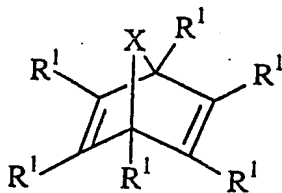
17. A method according to claim 16 wherein the metathesizable material  
comprises a cycloolefin.

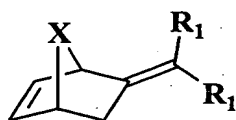
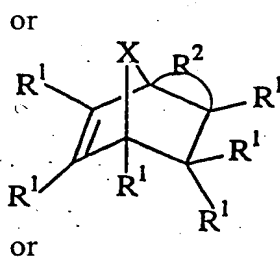
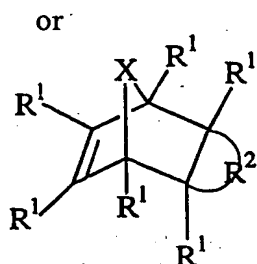
18. A method according to claim 17 wherein the metathesizable material is a  
20 monomer or oligomer selected from norbornene, cycloalkene, cycloalkadiene,  
cycloalkatriene, cycloalkatetraene, aromatic-containing cycloolefin and mixtures thereof.

19. A method according to claim 18 wherein the metathesizable material has a  
structure represented by



or





wherein X is  $\text{CH}_2$ ,  $\text{CHR}^3$ ,  $\text{C}(\text{R}^3)_2$ , O, S,  $\text{N-R}^3$ ,  $\text{P-R}^3$ ,  $\text{O=P-R}^3$ ,  $\text{Si}(\text{R}^3)_2$ ,  $\text{B-R}^3$  or  $\text{As-R}^3$ ; each  $\text{R}^1$  is independently H,  $\text{CH}_2$ , alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, alkaryl, aralkyl, halogen, halogenated alkyl, halogenated alkenyl, alkoxy, oxyalkyl, carboxyl, carbonyl, amido, (meth)acrylate-containing group, anhydride-containing group, thioalkoxy, sulfoxide, nitro, hydroxy, keto, carbamato, sulfonyl, sulfinyl, carboxylate, silanyl, cyano or imido;  $\text{R}^2$  is a fused aromatic, aliphatic or heterocyclic or polycyclic ring; and  $\text{R}^3$  is alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, alkaryl, aralkyl or alkoxy..

20. A method according to claim 17 wherein the metathesizable material comprises ethylidenenorbornene monomer or oligomer, dicyclopentadiene or bicyclo[2.2.1]hept-5-en-2-yl-trichlorosilane.

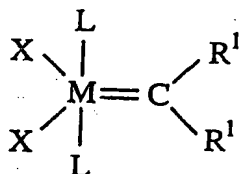
21. A method for bonding a fibrous substrate to an elastomeric substrate comprising:

- (a) applying a catalyst on the fibrous substrate;
- (b) contacting the catalyst on the fibrous substrate with a metathesizable material so that the metathesizable material undergoes a metathesis reaction;
- (c) contacting the fibrous substrate with the elastomeric substrate to form a

composite material; and

(d) curing said composite material.

22. A method according to claim 21 wherein the catalyst has a structure represented by



- wherein M is Os, Ru or Ir; each R<sup>1</sup> is the same or different and is H, alkenyl, alkynyl, alkyl, aryl, alkaryl, aralkyl, carboxylate, alkoxy, allenylidenyl, indenyl, alkylalkenylcarboxy, alkenylalkoxy, alkenylaryl, alkynylalkoxy, aryloxy, alkoxycarbonyl, alkylthio, alkylsulfonyl, alkylsulfinyl, amino or amido; X is the same or different and is either an anionic or a neutral ligand group; and L is the same or different and is a neutral electron donor group.

23. A method according to claim 22 wherein X is Cl, Br, I, F, CN, SCN, N<sub>3</sub>, O-alkyl or O-aryl; L is a heterocyclic ring or Q(R<sup>2</sup>)<sub>a</sub> wherein Q is P, As, Sb or N; R<sup>2</sup> is H, cycloalkyl, alkyl, aryl, alkoxy, arylate, amino, alkylamio, arylamino, amido or a heterocyclic ring; and a is 1, 2 or 3; M is Ru; and R<sup>1</sup> is H, phenyl, -CH=C(phenyl)<sub>2</sub>, -CH=C(CH<sub>3</sub>)<sub>2</sub> or -C(CH<sub>3</sub>)<sub>2</sub>(phenyl).

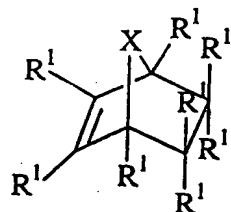
24. A method according to claim 21 wherein the catalyst is a phosphine-substituted, an imidazolylidene-substituted, or a dihydroimidazolylidene-substituted ruthenium carbene.

25. A method according to claim 24 wherein the catalyst is bis(tricyclohexylphosphine)benzylidene ruthenium (IV) dichloride, tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene][benzylidene]ruthenium (IV) dichloride, or tricyclohexylphosphine[1,3-bis(2,3,6-trimethylphenyl)-4,5-imidazol-2-ylidene][benzylidene]ruthenium (IV) dichloride.

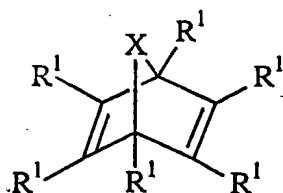
26. A method according to claim 21 wherein the metathesizable material comprises a cycloolefin.

27. A method according to claim 26 wherein the metathesizable material is a monomer or oligomer selected from norbornene, cycloalkene, cycloalkadiene, cycloalkatriene, cycloalkatetraene, aromatic-containing cycloolefin and mixtures thereof.

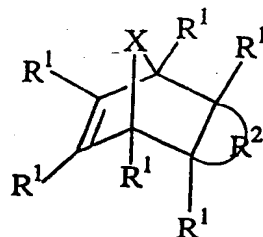
5 28. A method according to claim 27 wherein the metathesizable material comprises a norbornene having a structure represented by



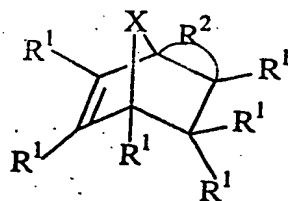
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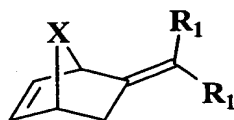
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or



or



wherein X is  $\text{CH}_2$ ,  $\text{CHR}^3$ ,  $\text{C}(\text{R}^3)_2$ , O, S,  $\text{N-R}^3$ ,  $\text{P-R}^3$ ,  $\text{O=P-R}^3$ ,  $\text{Si}(\text{R}^3)_2$ ,  $\text{B-R}^3$  or  $\text{As-R}^3$ ; each  $\text{R}^1$  is independently H,  $\text{CH}_2$ , alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, alkaryl, aralkyl, halogen, halogenated alkyl, halogenated alkenyl, alkoxy, oxyalkyl, carboxyl, carbonyl, amido, (meth)acrylate-containing group, anhydride-containing group, thioalkoxy, sulfoxide, nitro, hydroxy, keto, carbamato, sulfonyl, sulfinyl, carboxylate, silanyl, cyano or imido;  $\text{R}^2$  is a fused aromatic, aliphatic or heterocyclic or polycyclic ring; and  $\text{R}^3$  is alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, alkaryl, aralkyl or alkoxy.

29. A method according to claim 26 wherein the metathesizable material comprises ethylenenorbornene monomer or oligomer, dicyclopentadiene or bicyclo[2.2.1]hept-5-en-2-yl-trichlorosilane.

30. A method according to claim 21 wherein the fibrous substrate is polyester, nylon or polyamide.

31. A method according to claim 30 wherein the second substrate surface is selected from the group consisting of natural rubber, polychloroprene, polybutadiene, polyisoprene, styrene-butadiene copolymer rubber, acrylonitrile-butadiene copolymer rubber, ethylene-propylene copolymer rubber, ethylene-propylene-diene terpolymer rubber, butyl rubber, brominated butyl rubber, alkylated chlorosulfonated polyethylene rubber, hydrogenated nitrile rubber, silicone rubber, fluorosilicone rubber, poly(n-butyl acrylate), thermoplastic elastomer and mixtures thereof.

32. A method according to claim 31 wherein the elastomeric substrate is natural rubber or ethylene-propylene-diene terpolymer rubber.

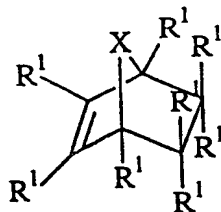
33. A method according to claim 21 wherein steps (a) and (b) take place at room temperature.

34. A manufactured article produced by the method of claim 1.

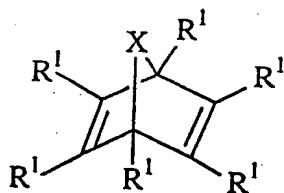
35. A manufactured article comprising a fibrous substrate sandwiched between and bonded to a second substrate surface and a third substrate and an adhesive layer interposed between the fibrous substrate and the second substrate and the third substrate wherein the second and third substrate comprise a rubber material and the adhesive layer comprises a metathesis polymer.

comprises a metathesis polymer.

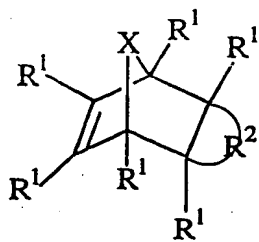
36. A manufactured article according to claim 35 wherein the metathesis polymer is produced from a norbornene monomer having a structure represented by



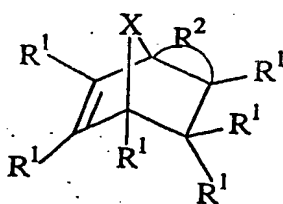
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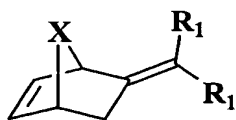
or



or



or



wherein X is  $\text{CH}_2$ ,  $\text{CHR}^3$ ,  $\text{C}(\text{R}^3)_2$ , O, S,  $\text{N-R}^3$ ,  $\text{P-R}^3$ ,  $\text{O=P-R}^3$ ,  $\text{Si}(\text{R}^3)_2$ ,  $\text{B-R}^3$  or  $\text{As-R}^3$ ; each  $\text{R}^1$  is independently H,  $\text{CH}_2$ , alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, alkaryl, aralkyl, halogen, halogenated alkyl, halogenated alkenyl, alkoxy, oxyalkyl, carboxyl, carbonyl, amido, (meth)acrylate-containing group, anhydride-containing group, thioalkoxy, sulfoxide, nitro, hydroxy, keto, carbamato, sulfonyl, sulfinyl, carboxylate, silanyl, cyano or imido;  $\text{R}^2$  is a fused aromatic, aliphatic or heterocyclic or polycyclic ring; and  $\text{R}^3$  is alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, alkaryl, aralkyl or alkoxy.

37. A manufactured article according to claim 35 wherein the metathesis polymer is produced from a norbornene monomer comprising ethylenenorbornene, dicyclopentadiene or bicyclo[2.2.1]hept-5-en-2-yl-trichlorosilane.

38. A method for providing a coating on a fibrous substrate comprising:

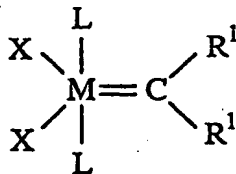
(a) providing a catalyst on the fibrous substrate; and

(b) contacting the catalyst on the fibrous substrate with a material that undergoes a metathesis reaction to form a coating on the fibrous substrate.

39. A method according to claim 38 wherein the catalyst is included as a component of the fibrous substrate.

40. A method according to claim 38 wherein the catalyst is selected from at least one of a rhenium compound, ruthenium compound, osmium compound, molybdenum compound, tungsten compound, titanium compound, niobium compound, iridium compound and  $\text{MgCl}_2$ .

41. A method according to claim 40 wherein the catalyst has a structure represented by



wherein M is Os, Ru or Ir; each  $\text{R}^1$  is the same or different and is H, alkenyl, alkynyl, alkyl, aryl, alkaryl, aralkyl, carboxylate, alkoxy, allenylidenyl, indenyl,

alkylalkenylcarboxy, alkenylalkoxy, alkenylaryl, alkynylalkoxy, aryloxy, alkoxycarbonyl, alkylthio, alkylsulfonyl, alkylsulfinyl, amino or amido; X is the same or different and is either an anionic or a neutral ligand group; and L is the same or different and is a neutral electron donor group.

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42. A method according to claim 41 wherein X is Cl, Br, I, F, CN, SCN, N<sub>3</sub>, O-alkyl or O-aryl; L is a heterocyclic ring or Q(R<sup>2</sup>)<sub>a</sub> wherein Q is P, As, Sb or N; R<sup>2</sup> is H, cycloalkyl, alkyl, aryl, alkoxy, arylate, amino, alkylamino, arylamino, amido or a heterocyclic ring; and a is 1, 2 or 3; M is Ru; and R<sup>1</sup> is H, phenyl, -CH=C(phenyl)<sub>2</sub>,  
10 -CH=C(CH<sub>3</sub>)<sub>2</sub> or -C(CH<sub>3</sub>)<sub>2</sub>(phenyl).

43. A method according to claim 40 wherein the catalyst is a phosphine-substituted, an imidazolylidene-substituted, or a dihydroimidazolylidene-substituted ruthenium carbene.

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44. A method according to claim 43 wherein the catalyst is bis(tricyclohexylphosphine)benzylidene ruthenium (IV) dichloride, tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene][benzylidene]ruthenium (IV) dichloride, or  
20 tricyclohexylphosphine[1,3-bis(2,3,6-trimethylphenyl)-4,5-imidazol-2-ylidene][benzylidene]ruthenium (IV) dichloride.

45. A method according to claim 38 wherein the metathesizable material is selected from ethene, α-alkene, acyclic alkene, acyclic diene, acetylene, cyclic alkene,  
25 cyclic polyene and mixtures thereof.

46. A method according to claim 45 wherein the metathesizable material is a monomer or oligomer selected from norbornene, cycloalkene, cycloalkadiene, cycloalkatriene, cycloalkatetraene, aromatic-containing cycloolefin and mixtures thereof.

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47. A method according to claim 38 wherein the metathesizable material comprises ethyridenenorbornene, dicyclopentadiene or bicyclo[2.2.1]hept-5-en-2-yl-trichlorosilane.

48. A method according to claim 38 wherein the fibrous substrate is fiberglass, polyester, polyamide or cotton.

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